

## 2-Bromo-*N'*-(*Z*)-2-bromobenzylidene]-5-methoxybenzohydrazide

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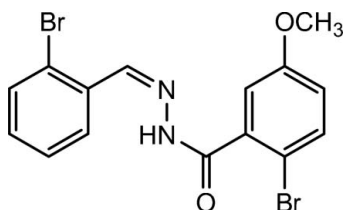
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}—\text{C}) = 0.007$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.122; data-to-parameter ratio = 18.0.

In the title compound,  $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2$ , the molecule adopts an *E* conformation about the  $\text{C}=\text{N}$  double bond and a *transoid* conformation about the central  $\text{N}—\text{N}$  bond, with a  $\text{C}(\text{=O})—\text{N}—\text{N}—\text{C}(\text{H})$  dihedral angle of  $169.4(4)^\circ$ . In the crystal, molecules are linked by  $\text{N}—\text{H}\cdots\text{O}$  hydrogen bonds, leading to  $C(4)$  chains. The packing also features slipped  $\pi—\pi$  stacking interactions, with a centroid-centroid separation of  $3.838(3)$  Å and a slippage of  $1.19$  Å.

### Related literature

For related structures and background, see: Narayana *et al.* (2007); Butcher *et al.* (2007).



### Experimental

#### Crystal data

$\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2$   
 $M_r = 412.09$   
 Monoclinic,  $P2_1/c$   
 $a = 14.768(5)$  Å  
 $b = 12.753(4)$  Å  
 $c = 8.227(3)$  Å  
 $\beta = 96.114(4)^\circ$

$V = 1540.6(9)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 5.27$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.30 \times 0.20 \times 0.20$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2006)  
 $T_{\min} = 0.301$ ,  $T_{\max} = 0.419$   
 (expected range = 0.251–0.349)

9369 measured reflections  
 3515 independent reflections  
 1902 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.063$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.122$   
 $S = 0.96$   
 3515 reflections  
 195 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.57$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.81$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$\text{N1}—\text{H1}\cdots\text{O1}^i$	0.87 (4)	2.07 (4)	2.906 (4)	160 (4)

Symmetry code: (i)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

HSY thanks the University of Mysore for research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2231).

### References

- Bruker (2006). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Butcher, R. J., Jasinski, J. P., Narayana, B., Sunil, K. & Yathirajan, H. S. (2007). *Acta Cryst. E* **63**, o3652.  
 Narayana, B., Siddaraju, B. P., Raju, C. R., Yathirajan, H. S. & Bolte, M. (2007). *Acta Cryst. E* **63**, o3522.  
 Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

## supporting information

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**2-Bromo-*N'*-[(*Z*)-2-bromobenzylidene]-5-methoxybenzohydrazide**

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**S1. Comment**

As part of our ongoing studies of substituted benzohydrazides (Narayana *et al.*, 2007; Butcher *et al.*, 2007) we now describe the synthesis and crystal structure of the title compound, (I) (Fig. 1).

The dihedral angle between the mean planes of the A (C1–C6) and B (C10–C15) rings is 18.6 (3)°. Atom C7 is displaced from the A plane by 0.064 (9) Å. The molecule is significantly twisted about the N1–N2 bond.

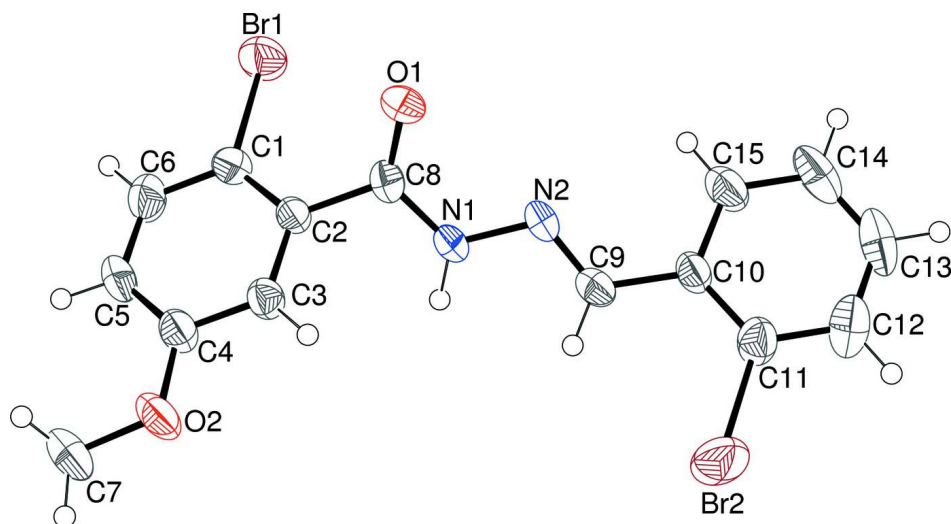
In the crystal, an intermolecular N—H···O interaction occurs (Table 2), leading to C(4) chains (Fig. 2) of molecules propagating in [001]. The shortest intermolecular aromatic ring centroid–centroid separation is 3.638 (3) Å, indicative of weak  $\pi$ - $\pi$  stacking.

**S2. Experimental**

A mixture of 2-bromobenzaldehyde (1.85 g, 0.01 mol) and 2-bromo-5-methoxybenzo-hydrazide (2.45 g, 0.01 mol) in 15 ml of ethanol containing 2 drops of 4 M hydrochloric acid was refluxed for 3 hours. On cooling, the solid separated was filtered and recrystallized from ethyl alcohol to yield colourless blocks of (I) (m.p: 440–442 K). Analysis (%) for C<sub>15</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: calculated (found): C 43.73 (43.66), H 2.94 (2.91), N 6.80 (6.76).

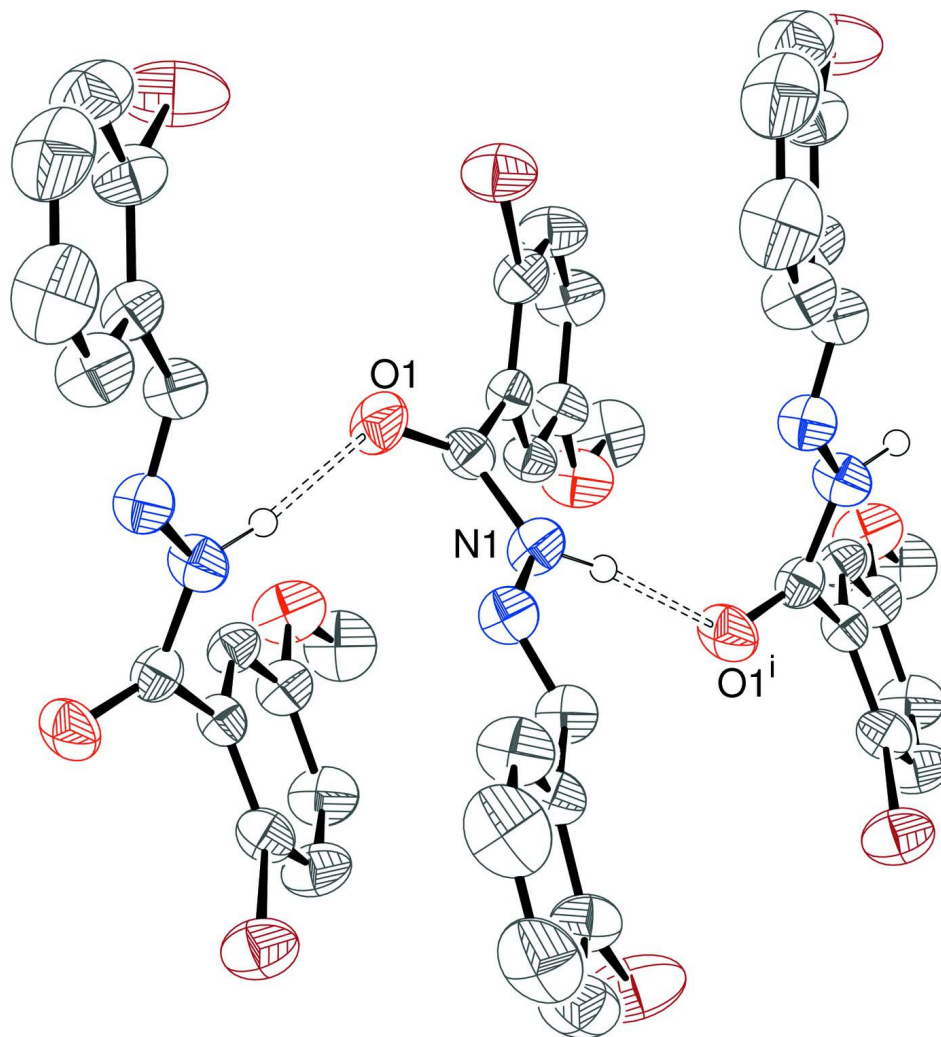
**S3. Refinement**

The N-bound H atom was located in a difference map and its position was freely refined. All the other H atoms were placed in idealized locations (C—H = 0.93–0.98 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . The methyl group was allowed to rotate, but not to tip, to best fit the electron density.



**Figure 1**

A view of (I) with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

**Figure 2**

A fragment of an [001] C(4) chain of molecules in the crystal of (I). Symmetry code as in Table 2.

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#### Crystal data

$C_{15}H_{12}Br_2N_2O_2$   
 $M_r = 412.09$   
 Monoclinic,  $P2_1/c$   
 Hall symbol: -P 2ybc  
 $a = 14.768$  (5) Å  
 $b = 12.753$  (4) Å  
 $c = 8.227$  (3) Å  
 $\beta = 96.114$  (4)°  
 $V = 1540.6$  (9) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 808$   
 $D_x = 1.777$  Mg m<sup>-3</sup>  
 Melting point = 440–442 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1776 reflections  
 $\theta = 2.8$ – $22.8^\circ$   
 $\mu = 5.27$  mm<sup>-1</sup>  
 $T = 296$  K  
 Block, colourless  
 $0.30 \times 0.20 \times 0.20$  mm

*Data collection*

Bruker SMART CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2006)  
 $T_{\min} = 0.301$ ,  $T_{\max} = 0.419$

9369 measured reflections  
3515 independent reflections  
1902 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.063$   
 $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.1^\circ$   
 $h = -19 \rightarrow 14$   
 $k = -12 \rightarrow 16$   
 $l = -10 \rightarrow 10$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.122$   
 $S = 0.96$   
3515 reflections  
195 parameters  
0 restraints  
Primary atom site location: structure-invariant  
direct methods  
Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$   
Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.0145 (10)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1558 (3)	0.0150 (3)	0.5766 (5)	0.0405 (11)
C2	0.1498 (3)	0.1213 (3)	0.5376 (5)	0.0322 (9)
C3	0.0842 (3)	0.1808 (3)	0.6039 (5)	0.0367 (10)
H3	0.0794	0.2520	0.5796	0.044*
C4	0.0256 (3)	0.1365 (3)	0.7055 (5)	0.0415 (11)
C5	0.0317 (3)	0.0314 (4)	0.7407 (6)	0.0536 (13)
H5	-0.0084	0.0006	0.8065	0.064*
C6	0.0973 (3)	-0.0282 (4)	0.6780 (6)	0.0522 (12)
H6	0.1024	-0.0990	0.7045	0.063*
C7	-0.0958 (3)	0.1633 (4)	0.8725 (6)	0.0655 (15)
H7A	-0.1332	0.1093	0.8189	0.098*
H7B	-0.1339	0.2188	0.9054	0.098*
H7C	-0.0608	0.1347	0.9672	0.098*
C8	0.2084 (3)	0.1719 (3)	0.4227 (5)	0.0356 (10)
C9	0.3247 (3)	0.4087 (4)	0.4401 (5)	0.0406 (10)

H9	0.2985	0.4355	0.5293	0.049*
C10	0.3904 (3)	0.4723 (3)	0.3608 (5)	0.0374 (10)
C11	0.3967 (3)	0.5806 (4)	0.3780 (6)	0.0477 (11)
C12	0.4617 (4)	0.6382 (4)	0.3079 (7)	0.0646 (15)
H12	0.4641	0.7107	0.3198	0.077*
C13	0.5223 (4)	0.5874 (5)	0.2207 (7)	0.0712 (17)
H13	0.5668	0.6254	0.1742	0.085*
C14	0.5179 (4)	0.4814 (5)	0.2017 (7)	0.0708 (16)
H14	0.5590	0.4475	0.1415	0.085*
C15	0.4530 (3)	0.4241 (4)	0.2707 (6)	0.0527 (13)
H15	0.4510	0.3517	0.2568	0.063*
Br1	0.24530 (3)	−0.07259 (4)	0.49919 (6)	0.0578 (2)
Br2	0.31365 (4)	0.65524 (4)	0.49486 (9)	0.0861 (3)
O1	0.2174 (2)	0.1358 (2)	0.2869 (3)	0.0489 (8)
O2	−0.0358 (2)	0.2037 (3)	0.7627 (4)	0.0579 (9)
N1	0.2468 (2)	0.2623 (3)	0.4809 (4)	0.0400 (9)
H1	0.239 (3)	0.277 (3)	0.582 (5)	0.048*
N2	0.3036 (2)	0.3173 (3)	0.3872 (4)	0.0391 (9)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.038 (3)	0.042 (3)	0.042 (3)	−0.002 (2)	0.011 (2)	−0.007 (2)
C2	0.030 (2)	0.037 (2)	0.030 (2)	−0.0044 (18)	0.0070 (18)	−0.0026 (18)
C3	0.038 (2)	0.036 (2)	0.038 (2)	0.0012 (19)	0.0104 (19)	0.0061 (19)
C4	0.036 (2)	0.046 (3)	0.044 (3)	0.000 (2)	0.012 (2)	0.003 (2)
C5	0.056 (3)	0.051 (3)	0.060 (3)	−0.010 (2)	0.034 (3)	0.004 (3)
C6	0.056 (3)	0.038 (3)	0.066 (3)	−0.005 (2)	0.020 (3)	0.008 (2)
C7	0.051 (3)	0.080 (4)	0.071 (4)	−0.002 (3)	0.035 (3)	0.000 (3)
C8	0.035 (2)	0.037 (3)	0.035 (2)	−0.0032 (19)	0.0082 (19)	0.007 (2)
C9	0.037 (2)	0.044 (3)	0.043 (3)	0.003 (2)	0.017 (2)	−0.001 (2)
C10	0.033 (2)	0.039 (3)	0.042 (2)	0.0010 (19)	0.0143 (19)	0.006 (2)
C11	0.037 (2)	0.043 (3)	0.064 (3)	−0.002 (2)	0.011 (2)	0.006 (2)
C12	0.057 (3)	0.056 (3)	0.080 (4)	−0.014 (3)	0.006 (3)	0.019 (3)
C13	0.055 (3)	0.091 (5)	0.070 (4)	−0.022 (3)	0.020 (3)	0.026 (3)
C14	0.051 (3)	0.100 (5)	0.068 (4)	0.001 (3)	0.035 (3)	0.012 (3)
C15	0.048 (3)	0.056 (3)	0.058 (3)	0.005 (2)	0.027 (2)	0.004 (2)
Br1	0.0569 (4)	0.0486 (3)	0.0713 (4)	0.0116 (2)	0.0227 (3)	−0.0006 (2)
Br2	0.0675 (4)	0.0502 (4)	0.1467 (7)	0.0080 (3)	0.0393 (4)	−0.0194 (4)
O1	0.066 (2)	0.050 (2)	0.0337 (17)	−0.0067 (16)	0.0203 (15)	−0.0084 (15)
O2	0.0502 (19)	0.059 (2)	0.071 (2)	0.0080 (17)	0.0370 (17)	0.0058 (18)
N1	0.044 (2)	0.045 (2)	0.035 (2)	−0.0083 (17)	0.0204 (18)	−0.0031 (18)
N2	0.039 (2)	0.044 (2)	0.038 (2)	−0.0050 (17)	0.0188 (16)	0.0016 (17)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—C6	1.378 (6)	C8—N1	1.350 (5)
C1—C2	1.394 (6)	C9—N2	1.272 (5)

C1—Br1	1.892 (4)	C9—C10	1.469 (6)
C2—C3	1.387 (5)	C9—H9	0.9300
C2—C8	1.495 (5)	C10—C15	1.388 (6)
C3—C4	1.386 (5)	C10—C11	1.390 (6)
C3—H3	0.9300	C11—C12	1.382 (6)
C4—O2	1.367 (5)	C11—Br2	1.894 (5)
C4—C5	1.373 (6)	C12—C13	1.369 (8)
C5—C6	1.375 (6)	C12—H12	0.9300
C5—H5	0.9300	C13—C14	1.361 (8)
C6—H6	0.9300	C13—H13	0.9300
C7—O2	1.427 (5)	C14—C15	1.375 (7)
C7—H7A	0.9600	C14—H14	0.9300
C7—H7B	0.9600	C15—H15	0.9300
C7—H7C	0.9600	N1—N2	1.388 (4)
C8—O1	1.229 (5)	N1—H1	0.87 (4)
C6—C1—C2	120.0 (4)	N2—C9—C10	120.3 (4)
C6—C1—Br1	118.2 (3)	N2—C9—H9	119.9
C2—C1—Br1	121.8 (3)	C10—C9—H9	119.9
C3—C2—C1	118.2 (3)	C15—C10—C11	116.9 (4)
C3—C2—C8	119.2 (4)	C15—C10—C9	120.1 (4)
C1—C2—C8	122.6 (3)	C11—C10—C9	122.9 (4)
C4—C3—C2	121.4 (4)	C12—C11—C10	121.9 (4)
C4—C3—H3	119.3	C12—C11—Br2	117.4 (4)
C2—C3—H3	119.3	C10—C11—Br2	120.7 (3)
O2—C4—C5	124.8 (4)	C13—C12—C11	119.2 (5)
O2—C4—C3	115.6 (4)	C13—C12—H12	120.4
C5—C4—C3	119.6 (4)	C11—C12—H12	120.4
C4—C5—C6	119.6 (4)	C14—C13—C12	120.3 (5)
C4—C5—H5	120.2	C14—C13—H13	119.9
C6—C5—H5	120.2	C12—C13—H13	119.9
C5—C6—C1	121.2 (4)	C13—C14—C15	120.5 (5)
C5—C6—H6	119.4	C13—C14—H14	119.7
C1—C6—H6	119.4	C15—C14—H14	119.7
O2—C7—H7A	109.5	C14—C15—C10	121.2 (5)
O2—C7—H7B	109.5	C14—C15—H15	119.4
H7A—C7—H7B	109.5	C10—C15—H15	119.4
O2—C7—H7C	109.5	C4—O2—C7	118.1 (4)
H7A—C7—H7C	109.5	C8—N1—N2	119.4 (3)
H7B—C7—H7C	109.5	C8—N1—H1	115 (3)
O1—C8—N1	124.1 (4)	N2—N1—H1	125 (3)
O1—C8—C2	122.7 (4)	C9—N2—N1	114.5 (3)
N1—C8—C2	113.2 (4)		
C6—C1—C2—C3	0.2 (6)	N2—C9—C10—C11	160.4 (4)
Br1—C1—C2—C3	−177.8 (3)	C15—C10—C11—C12	0.5 (7)
C6—C1—C2—C8	−177.3 (4)	C9—C10—C11—C12	177.2 (4)
Br1—C1—C2—C8	4.7 (6)	C15—C10—C11—Br2	178.8 (3)

C1—C2—C3—C4	−0.3 (6)	C9—C10—C11—Br2	−4.4 (6)
C8—C2—C3—C4	177.2 (4)	C10—C11—C12—C13	−0.8 (8)
C2—C3—C4—O2	180.0 (4)	Br2—C11—C12—C13	−179.2 (4)
C2—C3—C4—C5	−0.6 (7)	C11—C12—C13—C14	0.8 (8)
O2—C4—C5—C6	−179.0 (4)	C12—C13—C14—C15	−0.5 (9)
C3—C4—C5—C6	1.7 (7)	C13—C14—C15—C10	0.2 (8)
C4—C5—C6—C1	−1.8 (8)	C11—C10—C15—C14	−0.2 (7)
C2—C1—C6—C5	0.9 (7)	C9—C10—C15—C14	−177.0 (5)
Br1—C1—C6—C5	179.0 (4)	C5—C4—O2—C7	2.8 (7)
C3—C2—C8—O1	−127.5 (4)	C3—C4—O2—C7	−177.8 (4)
C1—C2—C8—O1	50.0 (6)	O1—C8—N1—N2	−2.9 (6)
C3—C2—C8—N1	50.2 (5)	C2—C8—N1—N2	179.5 (3)
C1—C2—C8—N1	−132.4 (4)	C10—C9—N2—N1	174.9 (4)
N2—C9—C10—C15	−23.0 (7)	C8—N1—N2—C9	169.4 (4)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O1 <sup>i</sup>	0.87 (4)	2.07 (4)	2.906 (4)	160 (4)

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2.